

Reaction of $[\text{Ru}_5(\mu_3\text{-CCH}_2)(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}]$ with $[\text{Fe}_2(\text{CO})_9]$. Formation of a Novel μ_4 -Vinylidene Ligand

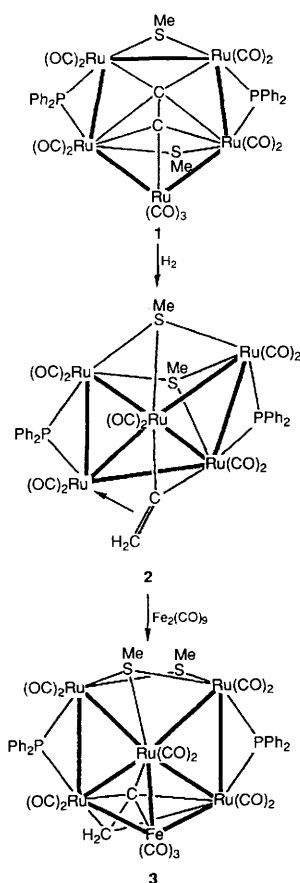
Chris J. Adams,^a Michael I. Bruce,^a Brian W. Skelton^b and Allan H. White^b

^a Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001

^b Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6009

The reaction between $[\text{Ru}_5(\mu_3\text{-CCH}_2)(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}]$ and $[\text{Fe}_2(\text{CO})_9]$ afforded the electron-rich mixed-metal cluster $[\text{FeRu}_5(\mu_4\text{-CCH}_2)(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_{13}]$, with a symmetrical μ_4 -vinylidene ligand; the metal core consists of an Ru_5 bow-tie, the central and two wing-tip atoms of which are attached to the Fe atom.

The pentagonal Ru_5 cluster $[\text{Ru}_5(\mu_5\text{-C}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{11}]$ **1** (Scheme 1) reacts with dihydrogen to form the



Scheme 1

electron-rich (80 cluster valence electrons) vinylidene cluster $[\text{Ru}_5(\mu_3\text{-CCH}_2)(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}]$ **2**.¹ We were interested to find out how the electron-rich nature of **2**, which is manifested in long Ru–Ru bonds, presumably because the extra four electrons are accommodated in Ru–Ru anti-bonding

orbitals, affected its reactivity. An early experiment involved its reaction with $[\text{Fe}_2(\text{CO})_9]$, from which we have obtained in moderate yield the hexanuclear vinylidene complex $[\text{FeRu}_5(\mu_4\text{-CCH}_2)(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_{13}]$ **3**.

The reaction between **2** (0.037 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (0.54 mmol) was carried out in toluene (10 cm³) for 48 h at 110 °C; separation by TLC gave black **3** as the major isolable crystalline product (40% yield). Analysis indicated the composition **2** + $\text{Fe}(\text{CO})_3$, although its precise nature was not immediately apparent from the spectroscopic data.* Accordingly, the solid-state structure was determined by an X-ray study.†

A molecule of **3** is depicted in Fig. 1. The non-planar hexanuclear FeRu_5 core consists of four fused triangles, in plan-view a centred pentagon with one of the peripheral bonds missing, but better considered as a bent Ru_5 'bow-tie', the central and two wing-tip atoms of which are attached to the Fe

* Selected analytical and spectroscopic data for **3**: Found: C, 34.05; H, 2.05%; M^+ , 1417. $\text{C}_{41}\text{H}_{28}\text{FeO}_{13}\text{P}_2\text{Ru}_5\text{S}_2$ requires C, 34.80; H, 2.00%; M , 1417. IR: $\nu(\text{CO})$ (cyclohexane) 2060s, 2037vs, 2028 (sh), 2023vs, 2013w, 2002m, 1996s, 1976m, 1966s, 1948w cm^{-1} . NMR (CDCl_3): ^1H , δ 1.14 (3 H, s, SMe), 1.89 (1 H, t, J_{HP} 4.4, CCH), 2.50 (1 H, s, CCH), 3.50 (3 H, t, J_{HP} 2.1, SMe), 6.98–7.03 (6 H, m, Ph), 7.33–7.48 (10 H, m, Ph), 7.70–7.77 (4 H, m, Ph); ^{13}C , δ 18.13, 21.47 (2 \times s, SMe), 27.76 (s, CH_2), 127.57–133.11 (m, Ph), 137.62 (d, J_{CP} 30.5, ipso C), 140.94 (d, J_{CP} 36.01, ipso C), 188.60 (s, CO), 190.82 (d, J_{CP} 9.7, CO), 193.55 (d, J_{CP} 10.6, CO), 194.94 (d, J_{CP} 3.4, CO), 195.69 (d, J_{CP} 3.5 Hz, CO), 190.82 [s, $\text{Fe}(\text{CO})$]. Fast atom bombardment MS: m/z 1417, M^+ ; 1389–1053, $[M - n\text{CO}]^+$ ($n = 1$ –13).

† Crystal data: $\text{C}_{41}\text{H}_{28}\text{FeO}_{13}\text{P}_2\text{Ru}_5\text{S}_2$, $M = 1416.0$, orthorhombic, space group $Pcnb$ (variation of $Pbcn$), $a = 25.006(8)$, $b = 19.768(11)$, $c = 19.540(8)$ Å, $Z = 8$, $D_c = 1.95$ g cm^{-3} , $F(000) = 5488$. Crystal dimensions: $0.17 \times 0.17 \times 0.23$ mm, $\mu(\text{Mo-K}\alpha) = 18.6$ cm^{-1} , A^* (min., max.) = 1.34, 1.40 (Gaussian correction). 8551 Independent absorption-corrected reflections were measured at ca. 295 K within the limit $2\theta_{\text{max}} = 50^\circ$ using a Syntex P2₁ diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo-K α radiation, $\lambda = 0.71073$ Å), 3813 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. R, R' were 0.048, 0.042, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Core hydrogen atoms were located in the final difference map. Computation used the XTAL 2.6 program system² implemented by S. R. Hall; neutral-atom complex scattering factors were employed.

Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

A prior determination was undertaken on a specimen which, although isomorphous, was a dichloromethane hemisolvate, the carbon of the solvent being located on a crystallographic two-fold axis. The precision offered by the unsolvated form (above) was slightly superior and is recorded in the main text; details of the structure of the solvate (which in respect of the molecular core geometry does not deviate non-trivially from that of the unsolvated form) are also deposited.

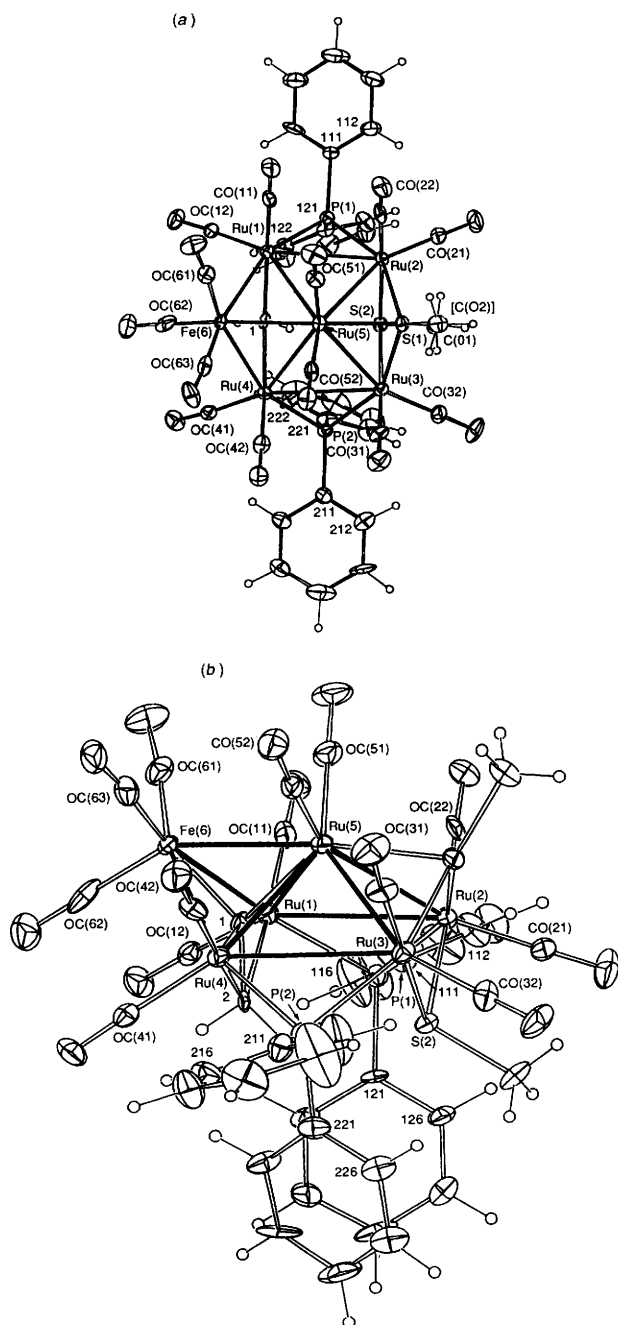


Fig. 1 Projections of a molecule of $[\text{FeRu}_5(\mu_4\text{-CCH}_2)(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_{13}]$ **3** (a) normal and (b) oblique to the Ru(1-4) 'plane' (χ^2 695; Ru deviations ± 0.02 Å), showing atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond parameters: Ru(1)-Ru(2) 3.201(2), Ru(1)-Ru(5) 3.002(2), Ru(1)-Fe(6) 2.882(2), Ru(2)-Ru(5) 3.037(2), Ru(2)⋯Ru(3) 3.714(2), Ru(3)-Ru(4) 3.239(2), Ru(3)-Ru(5) 3.026(2), Ru(4)-Ru(5) 2.983(2), Ru(4)-Fe(6) 2.874(2), Ru(5)-Fe(6) 2.721(2) and C(1)-C(2) 1.43(2) Å; dihedral Ru(4)-Ru(5)-Fe(6)/Ru(3)-Ru(4)-Ru(5) 79.17(5)°.

atom. One of the non-bonded Ru⋯Ru vectors is bridged by the two SMe groups, one of which also interacts with Ru(5); the other Ru⋯Ru vector is bridged by the CCH₂ ligand which is also bonded to Fe(6) and Ru(5) via C(1). The Ru-S bonds involving the μ-SMe ligand are longer [Ru(2,3)-S(2) 2.452(4), 2.445(4) Å] than those from the μ₃-SMe group [Ru(2,3,5)-S(1) 2.386(4), 2.372(4), 2.320(4) Å]. Peripheral Ru-Ru bonds from Ru(2) and Ru(3) are bridged by the μ-PPh₂ groups, the Ph

groups of which project to the side of and below the square plane. The iron atom has added to the Ru₅ system to bridge Ru(1) and Ru(4) [Ru(1,4)-Fe(6) 2.882(2), 2.874(2) Å], and is also attached to the central Ru(5) atom [Ru(5)-Fe(6) 2.721(2) Å]; in so doing, an FeRu₃ butterfly is formed, with the iron atom occupying a hinge position. The central Ru(5) atom is bonded to all other metal atoms; these bonds are, on average, 0.16 (to Fe) or 0.22 Å (to Ru) shorter than the corresponding peripheral bonds. Each Ru atom carries two CO groups, while the Fe atom has three.

The CCH₂ ligand is attached to the FeRu₃ butterfly so that C(1) is strongly bonded to all four metal atoms [Fe(6)-C(1) 1.85(1) Å; Ru(1,4,5)-C(1) 2.00(1), 2.05(1), 2.08(1) Å] and C(2) to the wing-tip atoms [Ru(1,4)-C(2) 2.33(1), 2.36(1) Å]. This structure represents a novel form of bonding of the CCH₂ ligand to four metal atoms, in that the C=C double bond appears to interact with both wing-tip atoms, rather than being canted towards one of them as in previous examples.³ In **3**, the coordination of C(1) is similar to that found in several complexes of the type $[\text{Fe}_4(\mu_4\text{-CR})(\text{CO})_{13}]$ (e.g., R = CO₂Me or C(OMe)₂; all derivatives of $[\text{Fe}_4(\mu_4\text{-C})(\text{CO})_{12}]^{2-}$);⁴ this type of carbon is restricted to bonding to C(sp²)-hybridised substituents.⁵

The ¹H NMR spectrum contains resonances at δ 1.89 and 2.50, assigned to the CCH₂ protons, while the ¹³C NMR spectrum contains a peak at δ 27.76 for the vinylidene CH₂ carbon; the other vinylidene carbon resonance was not found. The Me groups on the μ-SMe and μ₃-SMe groups are distinguished by resonances at δ 1.14 and 3.50, respectively.

The 94 cluster valence electron count for **3** is two electrons in excess of the number anticipated for a six-metal atom cluster with nine M-M bonds. This assumes that the vinylidene ligand contributes only four electrons. Thus, formally **3** is not as electron-rich as **2**; however, the lengthening of the M-M bonds found in the structure argues for the accommodation of the extra electrons in a M-M antibonding orbital, which would appear to extend over the whole of the metal framework. Lengthening of Ru-Ru bonds has been found previously in the electron-rich (64 electrons) planar Ru₄ clusters $[\text{Ru}_4(\mu\text{-PPh}_2)_2(\text{CO})_{13}]$ and $[\text{Ru}_4(\mu\text{-PPh}_2)_4(\text{CO})_{10}]$, where average lengths of PPh₂-bridged bonds are 3.160 and 3.050 Å, respectively.⁶ The Ru-Fe bonds in **3** are also longer than the average value of 2.697 Å found for five Fe-Ru clusters.⁷ A detailed theoretical study is necessary to elucidate the electron distribution in **2**, **3** and related molecules.

In conclusion, the reaction between **2** and $[\text{Fe}_2(\text{CO})_9]$ has given a very unusual type of vinylidene cluster, with an unprecedented M₆ geometry. It is clear that the chemistry of **1** and derived complexes is full of fascinating and unusual results, which are being vigorously pursued at present.

Acknowledgements

We thank the Australian Research Council for financial support and Johnson Matthey Technology Centre for a generous loan of RuCl₃·*n*H₂O.

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Received 13th July 1992; Communication 2/03680K